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(71) Applicant (for all designated States except US): **PLUG
POWER INC.** [US/US]; 968 Albany-Shaker Road,
Latham, NY 12110 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **LIEFTINK, Dick, J.**
[NL/NL]; Zevenwouden 192, NL-3524 CX Utrecht (NL).
DE WIT, Ellart, K. [NL/NL]; A. Menninckwartier 73,
NL-3554 CS Utrecht (NL). **DER KINDEREN, Joannes,
M.** [NL/NL]; Verdijkstraat 29, NL-7391 SJ Twello (NL).

(74) Agent: **HULETT, Joe, D.**; 20333 SH 249, Houston, TX
77070 (US).

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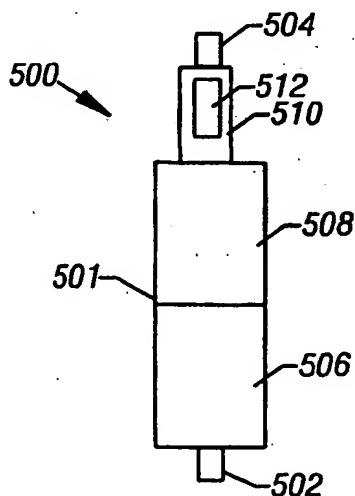
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ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: GAS PURIFICATION SYSTEM



(57) Abstract: Methods and apparatuses are provided for removing odorants, such as tetrahydrothiophene, and sulfur compounds, such as hydrogen sulfide, out of a gas, such as natural gas. Such systems are typically required by fuel processor systems, where the odorant and sulfur compounds might, otherwise, poison the fuel processor and fuel cell catalysts. Systems (500) of the present invention are based on the use of two filtration stages (506, 508) so that the odorant removal function is segregated from the general removal of hydrogen sulfide.

WO 03/099421 A1

[0016] The fuel cell stack may include flow plates (graphite composite or metal plates, as examples) that are stacked one on top of the other. The plates may include various surface flow channels and orifices to, as examples, route the reactants and products through the fuel cell stack. Several PEMs (each one being associated with a particular fuel cell) may be dispersed throughout the stack between the anodes and cathodes of the different fuel cells. Electrically conductive gas diffusion layers (GDLs) may be located on each side of each PEM to act as a gas diffusion media and in some cases to provide a support for the fuel cell catalysts. In this manner, reactant gases from each side of the PEM may pass along the flow channels and diffuse through the GDLs to reach the PEM. The PEM and its adjacent pair are often assembled together in an arrangement called a membrane electrode assembly (MEA).

[0017] A fuel cell system may include a fuel processor that converts a hydrocarbon (natural gas or propane, as examples) into a fuel flow for the fuel cell stack. For a given output power of the fuel cell stack, the fuel flow to the stack must satisfy the appropriate stoichiometric ratios governed by the equations listed above. Thus, a controller of the fuel cell system may monitor the output power of the stack and based on the monitored output power, estimate the fuel flow to satisfy the appropriate stoichiometric ratios. In this manner, the controller regulates the fuel processor to produce this flow, and in response to controller detecting a change in the output power, the controller estimates a new rate of fuel flow and controls the fuel processor accordingly.

[0018] The fuel cell system may provide power to a load, such as a load that is formed from residential appliances and electrical devices that may be selectively turned on and off to vary the power that is demanded by the load. Thus, the load may not be constant, but rather the power that is consumed by the load may vary over time and abruptly change in steps. For example, if the fuel cell system provides power to a house, different appliances/electrical devices of the house may be turned on and off at different times to cause the load to vary in a stepwise fashion over time.

streams, either to protect catalysts or for other reasons. For example, sulfur may be removed from combustion fuels to prevent formation of sulfur dioxide and other exhaust components that cause acid rain.

[0022] There is a continuing need for an arrangement and/or technique to desulfurize gas streams, and to address one or more of the issues discussed above.

SUMMARY

[0023] In general, the invention provides methods and associated apparatuses for removing odorant and sulfur compounds from a gas stream such as natural gas (e.g., removing such compounds to less than 50 parts per billion). As an example, such systems are typically required by fuel processor systems adapted to convert natural gas into reformat for use in fuel cell systems, where the odorant and sulfur compounds might otherwise poison the fuel processor and fuel cell catalysts. Systems under the present invention are based on the use of at least two filtration stages such that the odorant removal function is segregated from the general removal of H_2S . This advantageously enables the size and make-up of each stage to be tailored to a specific application. Some embodiments also provide modular systems allowing individual stages to be replaced independently as they become saturated with odorants and sulfur compounds. Other features and advantages are described herein.

[0024] As an example, whereas zeolite and activated carbon materials are often used to filter odorant and sulfur compounds from natural gas, the natural gas (sometimes referred to as "utility gas") in some areas of Europe, as an example, tends to contain levels of carbonyl sulfide (COS) and other components that are not absorbed by zeolites or activated carbon. In such systems, a second material such as nickel oxide may be required to remove materials such as COS. Such materials are typically expensive relative to more conventional absorbents such as zeolites and activated carbon. However, even in areas where difficult-to-absorb components like COS are present, levels are still generally low enough

greater than 10°C, wherein the third material is adapted to adsorb H₂S (e.g., a zeolite having a mean pore size less than 10 angstroms); and flowing the gas through the third material prior to contacting the gas with the first material.

[0027] Another step may include flowing the gas from the second material through a fourth material adapted to provide a visual indication of H₂S detection. Methods under the invention may also include: maintaining the first material at a first temperature; and maintaining the second material at a second temperature, wherein the first temperature is different from the second temperature. Other methods under the invention may also include: absorbing the odorant component into the first material; and replacing the first material with fresh first material while not replacing the second material. Still other methods under the invention may include: absorbing H₂S into the second material; and replacing the second material with fresh second material while not replacing the first material.

[0028] In another aspect, the invention provides an apparatus for removing sulfur compounds from a gas stream. The system includes a first material and a second material, and a conduit having an inlet and an outlet. The conduit provides fluid communication from the inlet to the first material, from the first material to the second material, and from the second material to the outlet (i.e., the gas flows along the conduit through each of the two stages). The first material is suitable for absorbing an odorant compound, and the second material is suitable for absorbing H₂S. The first material can comprise a zeolite, and the first material and second material can be different substances.

[0029] Advantages and other features of the invention will become apparent from the following description, drawing and claims.

DESCRIPTION OF THE DRAWINGS

[0030] Fig. 1 shows a flow diagram of a method of removing sulfur compounds from a gas stream.

[0031] Fig. 2 shows a flow diagram of a method of removing sulfur compounds from a gas stream.

[0037] The first material in compartment 302 is a material suitable for absorbing odorant compounds from the gas. As an example, where the gas is methane and contains sulfur-based odorants, the first material can be a type X zeolite or activated carbon, either in monolith or pellet form, as examples. Since it may also be necessary to remove COS and other compounds not absorbed by the first material, the second material is provided in the second compartment 308 as a second filtration stage. As an example, nickel materials (e.g., NiO) are suitable materials. The second material can also be another zeolite. For example, where CO₂ is present in the gas stream and a type X zeolite is used as the first material, the CO₂ can react in the pores of the zeolite with H₂S to form COS. To prevent such COS formation, a zeolite may be selected as the second material that has a pore size small enough (e.g., smaller than 10 angstroms) to prevent CO₂ from being absorbed.

[0038] As previously mentioned, one aspect of the invention is that with multiple filtration stages, it may be possible to replace individual vessel compartments or materials (e.g., at service intervals) without having to replace the entire de-sulfurization vessel. The individual compartments and/or the capacity of the material quantities provided in the vessel can also be tailored to a given application. Another feature of the invention may include an electric heater associated with the first material to heat the first material up during a cold start (e.g., below 20°C or 0°C, as examples). It will be appreciated that the effectiveness of various materials to absorb gas components may be diminished at relatively low temperatures. Without such an arrangement, the start-up time of a system may be prolonged while the de-sulfurization bed heats up with the rest of the system.

[0039] As another example, a cold-start module (not shown) may be associated with any of the systems described herein (e.g., 300, 400, 500). In such a cold start module, an electric heater can be activated to provide heat to an adsorption material that is only used during start-up. For example, a small quantity of a highly active, less-temperature dependent material such as nickel can be used in

compartment 506 containing a first material, and a second compartment 508 containing a second material. A third compartment 510 is positioned between the second compartment 508 and the outlet 504. The third compartment contains a third material and includes a window 512.

[0043] The third material is selected to provide a visual indication when contacted with sulfur compounds. As an example, the gas may be passed through a material containing lead acetate as it exits the vessel 501 through outlet 504. As known in the art, lead acetate, which is normally white, will turn black when contacted with sulfur compounds as it is converted to lead sulfide. Other suitable materials are known in the art. This visual indication can be observed through window 512. In this way, the system 500 provides a visual indication of when sulfur begins "breaking through". In other words, a visual indication is provided that the absorbent materials in the system need to be refreshed or replaced (e.g., a service call).

[0044] While the invention has been disclosed with respect to a limited number of embodiments, those skilled in the art, having the benefit of this disclosure, will appreciate numerous modifications and variations therefrom. It is intended that the invention covers all such modifications and variations as fall within the true spirit and scope of the invention.

lanthanide oxide, alumina, ceria, molybdenum oxide, vanadium oxide, manganese oxide, cobalt oxide, iron oxide and nickel oxide.

8. The method of claim 7, further comprising:
heating a third material to a temperature greater than 10°C, wherein the third material is adapted to adsorb H₂S; and
flowing the gas through the third material prior to contacting the gas with the first material.
9. The method of claim 1, further comprising:
flowing the gas from the second material through a fourth material adapted to provide a visual indication of H₂S detection.
10. The method of claim 1, further comprising:
maintaining the first material at a first temperature; and
maintaining the second material at a second temperature, wherein the first temperature is different from the second temperature.
11. The method of claim 1, further comprising:
absorbing the odorant component into the first material; and
replacing the first material with fresh first material while not replacing the second material.
12. The method of claim 1, further comprising:
absorbing H₂S into the second material; and
replacing the second material with fresh second material while not replacing the first material.
13. The method of claim 1, further comprising:
flowing the gas through a cold-start material comprising nickel during a system start-up step;

lanthanide oxide, alumina, ceria, molybdenum oxide, vanadium oxide, manganese oxide, cobalt oxide, iron oxide and nickel oxide.

20. The apparatus of claim 19 further comprising a third material adapted to receive a flow of the gas stream from the second material, wherein the third material is a zeolite material having a mean pore size less than 10 angstroms.

21. The apparatus of claim 14, further comprising an electric heater adapted to selectively heat the first material.

22. An apparatus for removing sulfur compounds from a gas stream, comprising:
a first stage and a second stage;
a conduit having an inlet and an outlet, the conduit providing fluid communication from the inlet to the first stage, from the first stage to the second stage, and from the second stage to the outlet;
wherein the first stage comprises a zeolite material; and
wherein the second stage comprises a material selected from the group comprising H₂S absorbents and COS hydrolysis catalysts.

23. The apparatus of claim 22, wherein the first stage is removeably connected to the conduit, and wherein the second stage is removeably connected to the conduit.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : Please See Continuation Sheet

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,460,533 A (DESCHAMPS et al.) 17 July 1984 (17.06.1984), please see column 1 lines 6-37 and column 2 lines 45 to column 3 line 21.	1, 4, 5, 14, 16 and 17
Y	US 4,359,450 A (BLYTAS et al.) 16 November 1982 (16.11.1982), please see column 2 lines 6-30, column 4 lines 40-41 and column 6 lines 27-37.	1, 4, 5, 8-12, 14, 16, 17 and 21 6, 7, 18 and 19

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

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Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703)305-3230

Authorized officer

Timothy Vanooy

Telephone No. 703-308-0561